

PATENT SPECIFICATION

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NO DRAWINGS

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 (32) Filed 13 Nov. 1968 in
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 (51) International Classification C09B 29/30, 43/18
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(54) WATER-SOLUBLE MONOAZO DYESTUFFS AND PROCESS FOR PREPARING THEM

(71) We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, *vermale*

PATENTS ACT 1949

SPECIFICATION NO 1289159

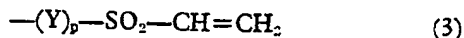
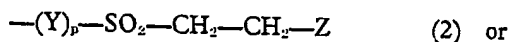
The following corrections were allowed under Section 76 on 15 September 1972

Page 3, line 16, for 965,121 read 965,902

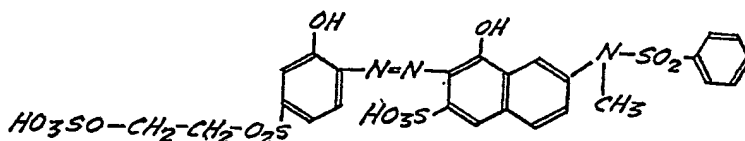
THE PATENT OFFICE
 17 October 1972

R 13854/54

10 wherein R and R' each represents an alkyl group or a phenyl group which may be substituted by one or more halogen atoms, alkyl, nitro, alkoxy or carboxy groups, Z₂ represents —CO— or —SO₂—, A and A' each represents a radical of the benzene or naphthalene series, Z₁ represents a bivalent bridging member, for example, —NH—CO—, —N(lower alkyl)—CO—, —CO—NH—, —CO—N(lower alkyl)—, —SO₂—NH—, —SO₂—N(lower alkyl)—, —NH—SO₂—, —N(lower alkyl)—SO₂—, —CO—, —SO₂—, —NH—, —S—, —O— or a lower alkylene group, X, being linked to A and/or A', represents one of the groupings 15



20 in which Z represents an inorganic or organic radical capable of being split off by an alkaline agent, Y represents the group —CH₂—, —CH₂—CH₂—, —NH— or —N(alkyl)— and m and p each represents the number 0 or 1, and n is 1 or 2, wherein the metal-free dyestuff of the formula 20



25 is excluded.
 The term "lower" as used in the specification refers to groups containing 1 to 4 carbon atoms. 25

[Price 25p]

SEE CORRECTION SLIP ATTACHED

NO DRAWINGS

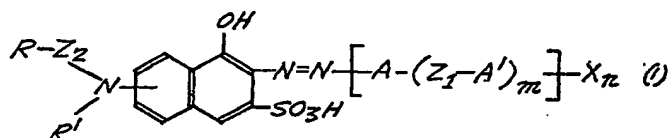
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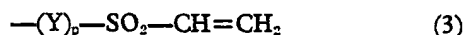
(54) WATER-SOLUBLE MONOAZO DYESTUFFS AND PROCESS
 FOR PREPARING THEM

(71) We, FARBWERKE HOECHST AKTIENGESSELLSCHAFT, vormals Meister Lucius & Brüning, a Body Corporate recognised under German Law, of 6230 Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

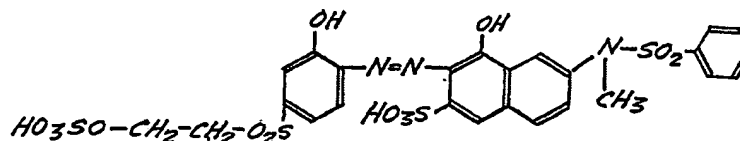
The present invention provides water-soluble monoazo dyestuffs which, in the form of the free acid, correspond to the general formula



wherein R and R' each represents an alkyl group or a phenyl group which may be substituted by one or more halogen atoms, alkyl, nitro, alkoxy or carboxy groups, Z₂ represents —CO— or —SO₂—, A and A' each represents a radical of the benzene or naphthalene series, Z₁ represents a bivalent bridging member, for example, —NH—CO—, —N(lower alkyl)—CO—, —CO—NH—, —CO—N(lower alkyl)—, —SO₂—NH—, —SO₂—N(lower alkyl)—, —NH—SO₂—, —N(lower alkyl)—SO₂—, —CO—, —SO₂—, —NH—, —S—, —O— or a lower alkylene group, X, being linked to A and/or A', represents one of the groupings



in which Z represents an inorganic or organic radical capable of being split off by an alkaline agent, Y represents the group —CH₂—, —CH₂—CH₂—, —NH— or —N(alkyl)— and m and p each represents the number 0 or 1, and n is 1 or 2, wherein the metal-free dyestuff of the formula



is excluded.

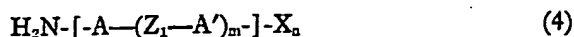
The term "lower" as used in the specification refers to groups containing 1 to 4 carbon atoms.

[Price 25p]

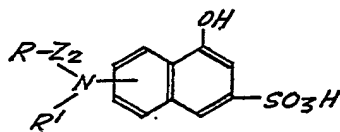
SEE CORRECTION SLIP ATTACHED

The present invention also provides a process for the preparation of said dyestuffs of the general formula 1 which comprises

a) coupling a diazotized aromatic amine having the general formula



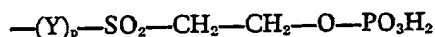
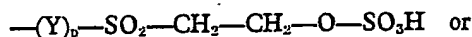
5 in which A, Z₁, A', X, m and n are defined as above with a coupling component of the formula



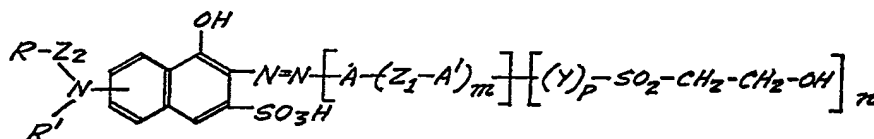
(5)

in which R, R' and Z₂ are defined as above, or

b) in as far as in the general formula (1) given above X represents in the final product the group



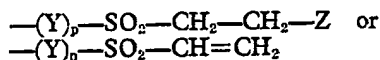
and Y and p are defined as above, converting a monoazo dyestuff of the general formula



(6)

wherein R, R', Z₂, A, A', Z₁, Y, m, n and p are defined as above by reaction with a sulphating or phosphorylating agent by a method known *per se* into the corresponding acid sulphuric acid ester or acid phosphoric acid ester.

The present invention especially provides dyestuffs of the above formula 1, wherein R represents a lower alkyl, phenyl, lower alkyl-phenyl, lower alkoxy-phenyl or di(lower alkoxy)-phenyl group, Z₂ represents a carbonyl or sulphonyl group, R' represents a lower alkyl, phenyl, carboxyphenyl, lower alkyl-phenyl, lower alkoxy-phenyl or di(lower alkoxy)phenyl group, A represents a phenylene, lower alkoxy-phenylene, lower alkyl-phenylene, di(lower alkoxy)phenylene or lower alkyl-lower alkoxy-phenylene group, Z₁ represents $-\text{CO}-\text{NH}-$ or $-\text{NH}-$, A' represents phenylene, nitrophenylene, or naphthylene, X, being linked to A or A', represents one of the groupings



in which Y represents $-\text{NH}-$ or $-\text{N}(\text{lower alkyl})$, Z represents a $-\text{SSO}_3\text{H}$, $-\text{OSO}_3\text{H}$, $-\text{O}-\text{PO}_3\text{H}_2$ or $-\text{N}(\text{lower alkyl})_2$ group, m and p each represents the number 0 or 1 and n is 1 or 2 and a process for preparing such dyestuffs.

The benzene or naphthalene nuclei A and A' may contain further substituents usual in azo dyestuffs, for example, alkyl, alkoxy, nitro, carboxy, hydroxy or sulphonic acid groups or halogen atoms. As the organic or inorganic radicals Z capable of being split off by an alkaline agent there may be mentioned by way of example a halogen atom, for example, a chlorine atom, an alkyl or arylsulphonic acid ester group or an acyloxy group, for example, an acetoxy group, moreover a phenoxy or dialkylamino group, a thiosulphuric acid- or phosphoric acid ester group or, more especially a sulphonic acid ester group.

The monoazo dyestuffs provided by the process of the present invention can be isolated by salting out, for example with sodium chloride or potassium chloride or by spray-drying the mixture obtained.

The new monoazo dyestuffs corresponding to the general formula 1 mentioned above are very suitable for the dyeing or printing of fibrous materials consisting, for example, of wool, silk, polyamide fibres, polyurethane fibres or, more especially, cellulose fibres, for example, cotton, natural or regenerated cellulose fibres or linen, or leather. They can be used for that purpose, advantageously, according to dyeing or printing methods commonly known in industry for reactive dyestuffs.

The present invention therefore provides a dyeing or printing process wherein a dyestuff of the present invention is used.

They yield on cellulosic fibrous materials, when applied in the presence of an alkaline agent, deep dyeings and prints which have good or very good fastness to light and to wet processing and are also distinguished by a good solubility.

In comparison with the monoazo dyestuffs described in German Patent Specifications 965,121 or 1,204,762 or those disclosed in the "Collection of Czechoslov. Chem. Commun." 27, 268—275 (1962) which dyestuffs have the most closely related structure the monoazo dyestuffs of the present invention are essentially superior with respect to the build up when applied according to dyeing or printing processes.

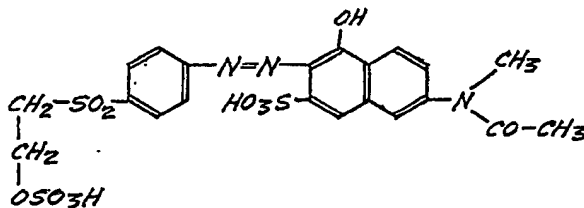
The following Examples illustrate the invention. The parts and percentages are by weight unless otherwise stated.

Example 1

50.6 parts of 2-methylamino-5-naphthol-7-sulphonic acid were introduced into 300 parts of water. To the mixture so-obtained, 25.8 parts of sodium hydroxide solution of 33% strength were added, whereby the 2-methyl-amino-5-naphthol-7-sulphonic acid dissolved. Subsequently, 30 parts of acetic acid anhydride were allowed to fall dropwise into the solution during a period of from 2 to 3 hours. The batch was stirred for three hours, 34.4 parts of a 33% sodium hydroxide solution were introduced, followed by 17.2 parts of anhydrous sodium carbonate and the batch was heated for 15 minutes to 90 to 95°C. at which temperature it was maintained for a further 15 minutes. After cooling to room temperature, the 2-(N-methyl-N-acetyl-amino)-5-naphthol-7-sulphonic acid solution was rendered neutral with about 32 parts of hydrochloric acid of 37% strength.

56.2 parts of 1-aminobenzene-4-β-hydroxyethyl-sulphone-sulphuric acid ester were introduced into a mixture of 200 parts of water and 200 parts of ice powder, mixed with 30 parts of hydrochloric acid of 37% strength and diazotised at 0 to 5°C. with 54.6 parts of sodium nitrite solution of 40% strength. To the said diazo suspension the above-mentioned 2-(N-methyl-N-acetyl-amino)-5-naphthol-7-sulphonic acid solution was added and the coupling mixture was neutralized by adding sodium carbonate. After stirring for a short time coupling was complete.

The dyestuff was precipitated with potassium chloride, separated by filtration and dried at 50 to 60°C. *in vacuo*. 138 parts of an orange powder were obtained which were soluble in water to give the same orange colour. The dyestuff, which in the form of the free acid, corresponded to the formula



yielded in the presence of an alkaline agent on natural or regenerated cellulose fibres clear orange dyeings or prints having a good fastness to wet and to light.

Example 2

40.2 parts of 1-aminobenzene-4-β-hydroxyethyl-sulphone were diazotized by a method known *per se*. Into the aqueous diazonium salt solution a neutral solution of 2-(N-methyl-N-acetyl-amino)-5-naphthol-7-sulphonic acid was allowed to run (prepared as described in the first paragraph of Example 1). The coupling mixture was rendered neutral by adding sodium carbonate and stirred until formation of the dyestuff was complete. The dyestuff was isolated by salting out with potassium chloride, filtered and dried at 70 to 80°C.

For conversion into its sulphuric acid ester the dyestuff was introduced, finely ground, into 600 parts of concentrated sulphuric acid and stirred until complete dissolution, whereupon the reaction mixture was poured onto 1,200 parts of ice powder. The dyestuff was precipitated with potassium chloride, filtered, washed to neutral with an aqueous potassium chloride solution of 20% strength and dried at 50 to 60°C., in a vacuum drying oven. It corresponded to the dyestuff obtained according to Example 1.

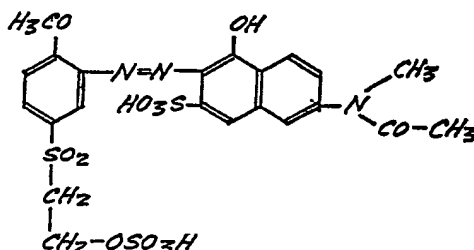
Example 3

58.7 parts of the dyestuff powder obtained according to the first paragraph of Example 1 were introduced into 250 parts of pyridine at the temperature of 85 to 90°C. Then 7.4 parts of urea and 42 parts of amido-sulphonic acid were added and the whole was heated for half an hour to 100 to 105°C. Subsequently, the mixture was poured onto 2,500 parts of water and the dyestuff isolated by salting out with potassium chloride. The precipitated dyestuff was filtered and the filter residue washed with aqueous potassium chloride solution.

The so-obtained product corresponded to the one produced according to Example 1 or 2.

Example 4

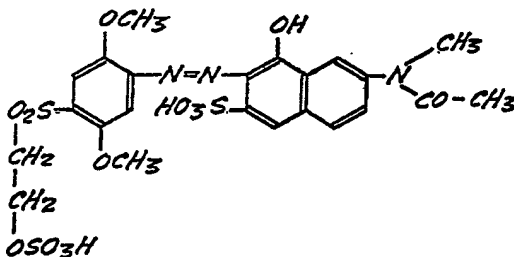
62.2 parts of 1-methoxy-2-aminobenzene-4,β-hydroxyethyl-sulphuric acid ester were diazotised in the manner described in the second paragraph of Example 1. To this diazo suspension a solution of 2-N-methyl-N-acetyl-amino-5-naphthol-7-sulphonic acid was added prepared from 50.6 parts of 2-methylamino-5-naphthol-7-sulphonic acid according to Example 1, paragraph 1 and the same procedure was then followed as described in said Example. Thus 141 parts of a red powder were obtained soluble in water while giving a red colour. The dyestuff corresponded in the form of the free acid to the formula



When used for dyeing or printing of cellulose fibres in the presence of an alkaline agent, it yielded clear, deep red dyeings which had good fastness to wet and to light.

Example 5

50.6 parts of 2-methylamino-8-naphthol-6-sulphonic acid were transformed into 2-(N-methyl-N-acetyl-amino)-8-naphthol-6-sulphonic acid in the manner described in the first paragraph of Example 1. The neutral solution was then coupled with a diazonium salt solution obtained by diazotising by a method known *per se* 68 parts of 2-amino-1,4-dimethoxybenzene-5-β-hydroxyethylsulphone-sulphuric acid ester. By adding sodium carbonate the coupling mixture was rendered weakly acid or neutral and stirred until coupling was complete. The dyestuff formed was precipitated with potassium chloride, filtered and dried at 50 to 60°C. in a vacuum drying oven. The dyestuff which was obtained as a red powder soluble in water while giving a red colour and corresponded in the form of the free acid to the formula

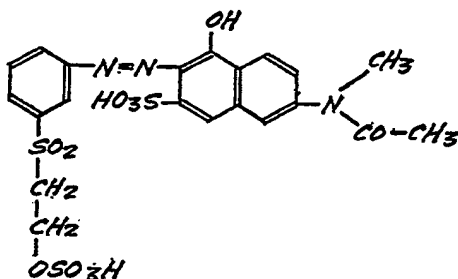


yielded on cellulose fibres in the presence of an alkaline agent deep red dyeings or prints having good fastness to light and to wet processing.

Example 6

56.2 parts of 1-amino-3- β -hydroxyethyl-sulphone-sulphuric acid ester were diazotised as described in Example 1, paragraph 2. Into the so-obtained aqueous diazo suspension a neutral 2-(N-methyl-N-acetylamino)-5-naphthol-7-sulphonic acid solution was allowed to run prepared in the manner of Example 1, paragraph 1 from 50.6 parts of 2-methylamino-5-naphthol-7-sulphonic acid. Subsequently, the coupling mixture was rendered weakly acid or neutral by means of sodium carbonate and the whole was stirred until the formation of the dyestuff was completed. The dyestuff was precipitated by adding potassium chloride, filtered and dried at 50 to 60°C. *in vacuo*.

135 parts of an orange powder were obtained soluble in water while giving an orange colour. The dyestuff, which in the form of the free acid, corresponded to the formula

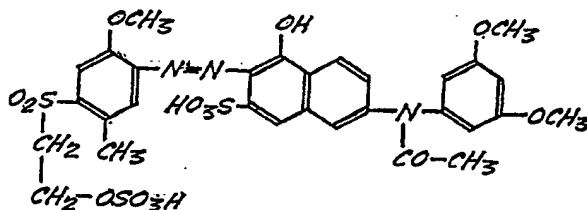


yielded in the presence of an alkaline agent, on natural or regenerated cellulose fibres orange dyeings or prints showing good fastness to light, wet processing and rubbing.

Example 7

37.5 parts of 2-(3',5'-dimethoxyphenylamino)-5-naphthol-7-sulphonic acid were introduced into 100 parts of acetic acid anhydride and refluxed for one hour. After cooling to room temperature, 200 parts of water were added and the whole was stirred for one hour. Subsequently, the batch was rendered to a pH-value of 7.0 to 7.5 with about 200 parts of 33% sodium hydroxide solution, 9 parts of anhydrous sodium carbonate were added and the whole was heated for 15 minutes to 90 to 95°C., cooled and rendered neutral with about 10 parts of concentrated hydrochloric acid.

This neutral 2-(N-3',5'-dimethoxyphenyl-N-acetyl-amino)-5-naphthol-7-sulphonic acid was coupled with a diazonium salt solution prepared by diazotising 1-methyl-3-amino-4-methoxy-benzene-6- β -hydroxyethyl-sulphone-sulphuric acid ester by a method known *per se*. The coupling mixture was rendered neutral by adding sodium carbonate and the whole was stirred until the formation of the dyestuff was completed. The dyestuff was precipitated with potassium chloride, filtered and dried at 50 to 60°C. in a vacuum drying oven. In the form of the free acid it corresponded to the formula



and was obtained as a red powder soluble in water, giving a red colour. In the presence of an alkaline agent it yielded on cellulose fibres deep red dyeings or prints possessing good fastness to wet and to light.

When instead of 37.5 parts of 2-(3',5'-dimethoxy-phenylamino)-5-naphthol-7-sulphonic acid, 35.9 parts of 2-(3'-carboxyphenylamino)-5-naphthol-7-sulphonic acid were used, a dyestuff with an analogous good fastness was obtained.

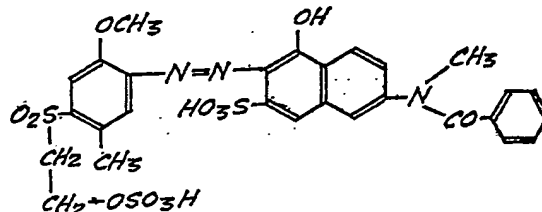
Example 8

25.3 parts of 2-methylamino-5-naphthol-7-sulphonic acid were stirred into 200 parts of water and the pH was adjusted to 5.8 to 6 by means of 20% sodium carbonate solution. Then 15.4 parts of benzoyl chloride were added dropwise to the mixture

during one hour while maintaining the pH between 5.8 and 6 by simultaneous dropwise addition of a 20% sodium carbonate solution.

The 2-(N-methyl-N-benzoylamino)-5-naphthol-7-sulphonic acid solution was, subsequently, added to a diazonium salt solution obtained by diazotisation of 1-methyl-3-amino-4-methoxybenzene-6- β -hydroxyethyl-sulphone-sulphuric acid ester. The coupling mixture was rendered neutral by means of sodium carbonate and the whole was stirred until the complete formation of the dyestuff. The dyestuff was precipitated by adding sodium chloride, filtered and dried at 50 to 60°C. in a vacuum drying oven.

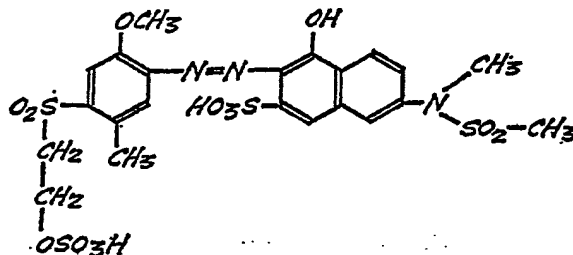
The resulting dyestuff was a red powder soluble in water, giving a red colour and which in the form of the free acid, corresponded to the formula



and yielded in the presence of sodium carbonate on natural or regenerated cellulose fibres deep red dyeings or prints having good fastness to wet and to light.

Example 9

25.3 parts of 2-methylamino-5-naphthol-7-sulphonic acid were dissolved in 200 parts of water and 32 parts of 33% sodium hydroxide solution at a pH between 6.5 and 7. Subsequently 12.8 parts of methanesulphonic acid chloride were added dropwise thereto while maintaining a pH between 5.8 and 6 by means of 20% sodium carbonate solution. 32.5 parts of 1-methyl-3-amino-4-methoxybenzene-6- β -hydroxyethyl-sulphone-sulphuric acid ester were diazotised by a method known *per se*. Into the diazonium salt solution the above-mentioned 2-(N-methyl-N-methylsulphonylamino)-5-naphthol-7-sulphonic acid was run and the coupling mixture was rendered weakly acid or neutral by means of sodium carbonate. The dyestuff which in the form of the free acid corresponded to the formula



was precipitated with potassium chloride, filtered and dried between 50 and 60°C. *in vacuo*.

When applied to fibrous materials consisting of cellulose in combination with a treatment by an acid binding agent, the dyestuff yielded red dyeings or prints very fast to wet and to light.

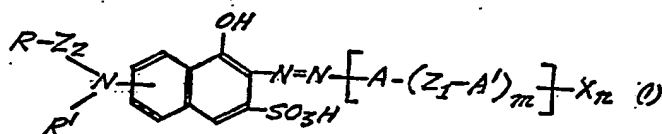
In an analogous manner as described in the preceding Examples the dyestuffs listed in the following Table could be obtained which also yielded on cellulose fibres dyeings or prints with similar good fastness properties.

	Coupling Component	Diazo Component	Shade
1	2-(N-methyl-N-acetyl-amino)-8-naphthol-6-sulphonic acid	1-aminobenzene-4- β -hydroxyethylsulphone-sulphuric acid ester	orange
2	— „ —	1-methoxy-2-aminobenzene-4- β -hydroxyethylsulphone-sulphuric acid ester	yellow-ish red
3	— „ —	1,4-dimethoxy-2-amino-benzene-5- β -hydroxy-ethyl-sulphone-sulphuric acid ester	red
4	— „ —	1-methyl-3-amino-4-methoxybenzene-6- β -hydroxyethylsulphone-sulphuric acid ester	red
5	— „ —	1-methyl-2-amino-4-methoxy-benzene-5- β -hydroxyethylsulphone-sulphuric acid ester	yellowish-red
6	— „ —	1-aminobenzene-3- β -hydroxyethyl-sulphone-sulphuric acid ester	orange
7	2-(N-phenyl-N-benzoyl-amino)-5-naphthol-7-sulphonic acid	1-methyl-3-amino-4-methoxy-benzene-6- β -hydroxyethylsulphone-sulphuric acid ester	red-brown
8	1-(N-methyl-N-acetyl-amino)-5-naphthol-7-sulphonic acid	1-aminobenzene-4- β -hydroxyethyl-sulphone-sulphuric acid ester	yellowish red
9	1-(N-methyl-N-acetyl-amino)-8-naphthol-6-sulphonic acid	1-aminobenzene-4- β -hydroxyethylsulphone-sulphuric acid ester	yellowish red

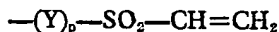
	Coupling Component	Diazo Component	Shade
10	2-(N-methyl-N-acetyl-amino)-8-naphthol-6-sulphonic acid	1-aminobenzene-4-vinyl-sulphone	orange
11	— „ —	1-methyl-3-amino-4-methoxybenzene-6- β -diethyl-aminoethylsulphone	red
12	— „ —	1-methyl-3-amino-4-methoxybenzene-6- β -thio-sulphatoethylsulphone	red
13	— „ —	1-methyl-3-amino-4-methoxybenzene-6- β -hydroxy-ethylsulphone-phosphoric acid ester	red
14	— „ —	4-(N-methyl-ethionyl-amino)-1-amino-benzene	orange
15	— „ —	3- <i>w</i> -(β -hydroxyethylsulphonyl)-methyl-1-aminobenzene-sulphuric acid ester	orange
16	— „ —	2-amino-naphthalene-5- β -hydroxyethylsulphone-sulphuric acid ester	red
17	— „ —	2-amino-naphthalene-4,8-di- β -hydroxyethylsulphone-acid ester	red
18	— „ —	4-ethionylamino-1-amino-benzene	orange
19	— „ —	β -hydroxyethyl-[3-(4'-aminobenzoylamino)-phenyl]-sulphone-sulphuric acid ester	orange
20	— „ —	β -hydroxyethyl-[4-(3'-aminophenylsulphonylamino)-phenyl]-sulphone-sulphuric acid ester	orange
21	— „ —	β -hydroxyethyl-[6-(4'-aminobenzoylamino)-naphthyl-(2)]-sulphone-sulphuric acid ester	orange
22	— „ —	4-amino-2'-nitro-di-phenylamino-4'- β -hydroxy-ethylsulphone-sulphuric acid ester	red

WHAT WE CLAIM IS:—

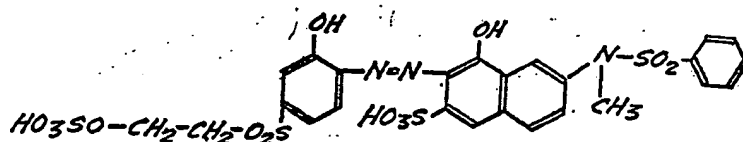
1. A water-soluble monoazo-dyestuff, which in the form of the free acid, corresponds to the general formula



wherein R and R' each represents an alkyl group or a phenyl group which may be substituted by one or more halogen atoms, alkyl-, nitro-, alkoxy- or carboxy groups, Z₂ represents —CO— or —SO₂—, A and A' each represents a radical of the benzene or naphthalene series, Z₁ represents a bivalent bridging member, X, being linked to A and/or A', represents one of the groupings

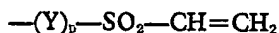


in which Z represents an inorganic or organic radical capable of being split off by an alkaline agent, and Y represents a group —CH₂—, —CH₂—CH₂—, —NH— or —N(alkyl)—, and m and p each represents the number 0 or 1, and n is 1 or 2, wherein the metal-free dyestuff of the formula



is excluded.

2. A water-soluble monoazo dyestuff as claimed in claim 1, wherein R represents a lower alkyl, phenyl, lower alkyl-phenyl, lower alkoxy-phenyl or di(lower alkoxy)-phenyl group, Z₂ represents a carbonyl or sulphonyl group, R' represents a lower alkyl, phenyl, carboxyphenyl, lower alkyl-phenyl, lower alkoxy-phenyl or di(lower alkoxy)phenyl group, A represents a phenylene, lower alkoxy-phenylene, lower alkyl-phenylene, di(lower alkoxy) phenylene or lower alkyl-lower alkoxy-phenylene group, Z₁ represents —CO—NH— or —NH—, A' represents phenylene, nitrophenylene, or naphthylene, X, being linked to A or A', represents one of the groupings

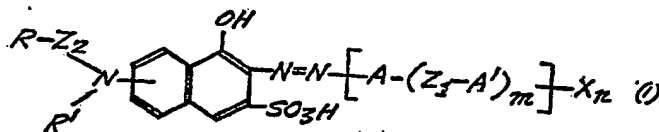


in which Y represents —NH— or —N(lower alkyl), Z represents a —OSO₃H, SSO₃H, —O—PO₃H₂ or —N(lower alkyl)₂ group, m and p each represents the number 0 or 1 and n is 1 or 2, and wherein "lower", as used with respect to alkyl and alkoxy groups, refers to such groups containing 1 to 4 carbon atoms.

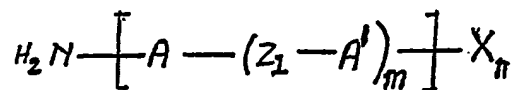
3. A water-soluble monoazo-dyestuff as claimed in claim 1, obtainable from any of the components specified herein substantially as described.

4. Any one of the water-soluble monoazo-dyestuffs as claimed in claim 1, obtainable as described in any one of the Examples or with reference to the Table herein.

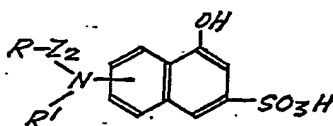
5. A process for the manufacture of water-soluble monoazo-dyestuffs, which, in the form of the free acid, correspond to the formula



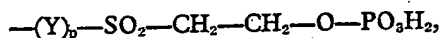
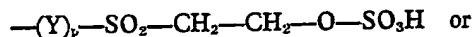
wherein R, R', Z₂, A, A', Z₁, X, n and m have the meanings given in claim 1, wherein a) a diazotised aromatic amine of the general formula



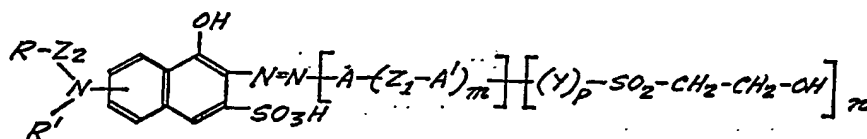
(4)
in which A, Z₁, A', X, m and n are defined as above, is coupled with a coupling component of the general formula



5 in which R, R' and Z₂ are defined as above, or
b) as far as in the general formula (1) given above X represents 5



Y and p being defined as above, a monoazo-dyestuff of the general formula



(6)
in which R, R', Z₂, A, A', Z₁, Y, m, n, and p are defined as above, is converted into the corresponding acid sulphuric acid ester or acid phosphoric acid ester, by reaction with a sulphating or phosphorylating agent.

6. A process as claimed in claim 5, wherein R, Z₂, R', Z₁, A', A, X, m and n have the meanings given in claim 2. 15

7. A process as claimed in claim 5 or 6 for the manufacture of water-soluble monoazo-dyestuffs from any of the components specified herein substantially as described. 20

8. A process as claimed in any one of claims 5 to 7 for the manufacture of water-soluble monoazo-dyestuffs conducted substantially as described in any one of the Examples or with reference to the Table herein. 25

9. Water-soluble monoazo-dyestuffs as claimed in claim 1, whenever prepared by a process claimed in any one of claims 5 to 8.

10. A process for dyeing or printing, wherein a dyestuff claimed in any of claims 1 to 4 or 9 is used. 30

11. A process for dyeing or printing as claimed in claim 10, conducted substantially as described and exemplified herein.

12. Leather or textile materials consisting of wool, silk, polyamide fibres, polyurethane fibres or natural or regenerated cellulose which have been dyed, printed or coloured by a process claimed in claim 10 or 11.

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